

What is claimed is:

1. A flexible, biaxially stretched, heat shrinkable polymeric film having at least one layer comprising a blend of at least three copolymers comprising:

20 to 85 weight percent of a first polymer having a melting point of 80 to 98°C comprising at least one copolymer of ethylene and hexene-1;

5 to 35 weight percent of a second polymer having a melting point of 115 to 128°C comprising at least one copolymer of ethylene and at least one α -olefin; and

10 to 50 weight percent of a third polymer having a melting point of 60 to 110°C comprising at least one copolymer of ethylene and a vinyl ester, an alkyl acrylate, acrylic acid, or methacrylic acid; wherein said first and second polymers have a combined weight percentage of at least 50 weight percent, said weight percentage being based upon the total weight of said first, second and third polymers; and wherein said film has a maximum ram puncture force of at least 70 Newtons, a ram puncture stress of at least 110 MPa, and a tear propagation strength "x" such that $10 \leq x \leq 40$ grams per mil in each of the machine and transverse directions or $x < 25$ grams per mil in at least one of the machine and transverse directions.

2. A film, as defined in claim 1, wherein said first polymer has a melting point of 80 to 92°C.

3. A film, as defined in claim 1, wherein said first polymer is a bipolymer.

4. A film, as defined in claim 1, wherein said first polymer is a terpolymer of: ethylene, butene-1 and hexene-1 or ethylene, hexene-1, octene-1.

5. A film, as defined in claim 1, wherein said second polymer comprises a copolymer of ethylene and octene-1.

6. A film, as defined in claim 1, wherein said third polymer is selected from the group of ethylene vinyl acetate copolymer, ethylene methylacrylate copolymer, ethylene butylacrylate copolymer, ethylene ethylacrylate copolymer, ethylene acrylic acid copolymer, and ethylene

543
B2
COP
methacrylic acid copolymer.

7. A film, as defined in claim 1, wherein said third polymer comprises a copolymer of ethylene and vinyl acetate.
8. A film, as defined in claim 1, further comprising a fourth polymer having a melting point of 80 to 110°C.
9. A film, as defined in claim 1, having a haze value of less than 10%.
10. A film, as defined in claim 1, wherein said film has a tear propagation strength of 15 to 25 g/mil in at least one of the machine and transverse directions.
11. A film, as defined in claim 1, wherein said film has a shrinkage value at 90°C of at least 45% in at least one of the machine and transverse directions.
12. A film, as defined in claim 1, wherein said film has a total energy at maximum puncture force of at least 0.60 Joule.
13. A film, as defined in claim 1, wherein said film has a total energy at maximum puncture force of at least 0.90 Joule.
14. A film, as defined in claim 1, wherein said film has a maximum ram puncture force of at least 90 Newtons.
15. A film, as defined in claim 1, wherein said film has a maximum ram puncture force of at least 100 Newtons.
16. A film, as defined in claim 1, wherein said film has a maximum ram puncture force of at least 110 Newtons.
17. A film, as defined in claim 1, wherein said film has a ram puncture stress of at least 140 MPa.
18. A film, as defined in claim 1, wherein said first polymer has a $\overline{M}_w/\overline{M}_n$ of 1.5 to 3.0.
19. A film, as defined in claim 1, wherein said first polymer has a $\overline{M}_w/\overline{M}_n$ of 2.2 to 2.6.
20. A film, as defined in claim 1, wherein said first polymer has a melt index of 1.5 to 3.0

dg/min..

21. A film, as defined in claim 1, wherein said first polymer has a melt index of 0.3 to 1.5 dg/min..

22. A film, as defined in claim 1, further comprising at least three additional polymeric layers.

23. A film, as defined in claim 1, wherein said blend containing layer has been irradiatively crosslinked.

24. A film, as defined in claim 1, wherein said layer is the innermost heat sealable layer of a tube formed of said film.

25. A film, as defined in claim 1, wherein said film is fabricated into bags.

26. A film, as defined in claim 1, further comprising a gas barrier layer and said film has an oxygen transmission rate of less than 15 cc/100 in² for 24 hrs. at 1 atm.

27. A film, as defined in claim 1, wherein said blend comprises at least 50 percent by weight of said layer based on the total weight of the layer.

28. A film, as defined in claim 1, wherein said first polymer is present in an amount of 25 to 45 weight percent, based upon the total weight of the first, second and third polymers.

29. A film, as defined in claim 1, wherein said first polymer is present in an amount of 30 to 40 weight percent, based upon the total weight of the first, second and third polymers.

30. A film, as defined in claim 1, wherein said first polymer is present in an amount of 45 to 85 weight percent, based upon the total weight of the first, second and third polymers.

31. A film, as defined in claim 1, wherein at least one of said first, second, and third polymers comprises an interpolymer.

32. A film, as defined in claim 1, wherein at least one interpolymer comprises said first and second polymers.

33. A film, as defined in claim 22, wherein said film comprises:

a first heat sealing surface layer comprising a polymer selected from the group consisting

of: (a) at least 50% by weight of a copolymer of propene and at least one α -olefin selected from the group consisting of ethylene, butene-1, methylpentene-1, hexene-1, octene-1 and mixtures thereof having a propene content of at least 60 wt. %, and (b) at least 50% by weight of a copolymer of ethylene and at least one α -olefin selected from the group consisting of propylene, butene-1, methylpentene-1, hexene-1, octene-1 and mixtures thereof having a melting point of at least 105°C and a density of at least 0.900 g/cm³;

a second intermediate layer;

a third core layer comprising at least 80% by weight (based on said third layer's weight) of at least one copolymer of vinylidene chloride with from 2 to 20 weight percent (based on said copolymer's weight) of vinyl chloride or methyl acrylate; and

a fourth surface layer;

wherein at least one of said second and said fourth layers comprise said three copolymer blend defined in claim 1, and said core layer is disposed between said second and said fourth layers.

34. A film, as defined in claim 33, wherein said film has a shrinkage value at 90°C of at least 40% in at least one of the machine and transverse directions.

35. A film, as defined in claim 33 or 34, wherein said film has a tensile seal strength of at least 400 g/cm at 88°C.

36. A film, as defined in claim 33, wherein said film has a tensile seal strength of at least 600 g/cm at 88°C.

37. A film, as defined in claim 33 or 34, wherein said film has a hot water puncture resistance value of at least 40 seconds at 95°C.

38. A film, as defined in claim 33, wherein said film has a hot water puncture resistance value of at least 100 seconds at 95°C.

39. A film, as defined in claim 33 or 34, wherein said film has an average hot water seal

strength of at least 200 seconds at 95°C.

40. A film, as defined in claim 33 or 34, wherein said film has an average hot water seal strength of at least 300 seconds at 95°C.

41. A film, as defined in claim 1 or 33, wherein said film has a ram puncture stress of at least 275 MPa..

42. A film, as defined in claim 33, wherein said melting point of said first heat sealing surface layer polymer (b) is at least 115°C.

43. A biaxially stretched, heat shrinkable film comprising at least three layers, wherein said first layer comprises a blend of at least three polymers comprising: a first polymer having a melting point of 80 to 98°C comprising a copolymer of ethylene and hexene-1; a second polymer having a melting point of 115 to 128°C comprising a copolymer of ethylene and at least one α -olefin; a third polymer having a melting point of 60 to 110°C comprising a copolymer ethylene and a vinyl ester or alkyl acrylate; a third layer comprising at least 50 percent by weight of copolymer of ethylene with at least one alpha-olefin or at least one vinyl ester or blends thereof, and a second layer comprising a vinylidene chloride copolymer, a nylon or a copolymer of ethylene with a vinyl alcohol; said film having a ram puncture force of at least 70 Newtons, a ram puncture stress of at least 110 MPa, and a tear propagation strength "x" such that $10 \leq x \leq 40$ grams per mil in each of the machine and transverse directions or $x < 25$ grams per mil in at least one of the machine and transverse directions.

44. A flexible, thermoplastic, biaxially stretched, heat shrinkable film having at least one layer comprising a blend of at least three copolymers comprising:

45 to 85 weight percent of a first polymer having a melting point of 80 to 98°C comprising at least one copolymer of ethylene and hexene-1;

5 to 35 weight percent of a second polymer having a melting point of 115 to 128°C comprising at least one copolymer of ethylene and at least one α -olefin; and

10 to 50 weight percent of a third polymer having a melting point of 60 to 110°C comprising at least one copolymer of ethylene and a vinyl ester or an alkyl acrylate; wherein said first and second polymers have a combined weight percentage of at least 50 weight percent, said weight percentage being based upon the total weight of said first, second and third polymers; and wherein said film has a maximum ram puncture force of at least 120 Newtons.

45. A film, as defined in claim 44, wherein said maximum puncture force is at least 150 Newtons.

46. A film, as defined in claim 44, wherein said maximum puncture force is at least 200 Newtons.

47. A film, as defined in claim 44, wherein said film has a total energy absorption of at least 1.20 Joules.

48. A film, as defined in claim 44, wherein said film has a total energy absorption of at least 1.50 Joules.

49. A film, as defined in claim 44, wherein said film has a total energy absorption of at least 2.0 Joules.

50. A film, as defined in claim 44, wherein said film has a maximum stress of at least 150 MPa..

51. A film, as defined in claim 44, wherein said film has a maximum stress of at least 275 MPa..

52. A film, as defined in claim 44, wherein at least one of said first, second, and third polymers comprises an interpolymer.

53. A film, as defined in claim 44, further comprising at least four additional thermoplastic layers.

54. A film, as defined in claim 44, wherein said film comprises:

a first heat sealing surface layer comprising a polymer selected from the group consisting of: (a) at least 50% by weight of a copolymer of propene and at least one α -olefin selected from

the group consisting of ethylene, butene-1, methylpentene-1, hexene-1, octene-1 and mixtures thereof having a propene content of at least 60 wt. %, and (b) at least 50% by weight of a copolymer of ethylene and at least one α -olefin selected from the group consisting of propylene, butene-1, methylpentene-1, hexene-1, octene-1 and mixtures thereof having a melting point of at least 105°C and a density of at least 0.900 g/cm³;

a second intermediate layer;

a third core layer comprising at least 80% by weight (based on said third layer's weight) of at least one copolymer of vinylidene chloride with from 2 to 20 weight percent (based on said copolymer's weight) of vinyl chloride or methyl acrylate; and

a fourth surface layer;

wherein at least one of said second and said third layers comprise said three copolymer blend defined in claim 44, and said core layer is disposed between said second and said fourth layers.

55. A film, as defined in claim 54, wherein said film has a shrinkage value at 90°C of at least 40% in at least one the machine and transverse directions.

56. A film, as defined in claim 54 or 55, wherein said film has a tensile seal strength of at least 400 g/cm at 88°C.

57. A film, as defined in claim 54, wherein said film has a tensile seal strength of at least 600 g/cm at 88°C.

58. A film, as defined in claim 54 or 55, wherein said film has a hot water puncture resistance value of at least 40 seconds at 95°C.

59. A film, as defined in claim 54, wherein said film has a hot water puncture resistance value of at least 100 seconds at 95°C.

60. A film, as defined in claim 54 or 55, wherein said film has an average hot water seal strength of at least 200 seconds at 95°C.

61. A film, as defined in claim 54 or 55, wherein said film has an average hot water seal strength of at least 300 seconds at 95°C.

62. A film, as defined in claim 54, wherein said film has a ram puncture stress of at least 275 MPa..

63. A film, as defined in claim 54, wherein said melting point of said first heat sealing surface layer polymer (b) is at least 115°C.

64. A biaxially stretched, heat shrinkable film comprising at least three layers, wherein said first layer comprises a blend of at least three polymers comprising: a first polymer having a melting point of 80 to 98°C comprising a copolymer of ethylene and hexene-1; a second polymer having a melting point of 115 to 128°C comprising a copolymer of ethylene and at least one α -olefin; a third polymer having a melting point of 60 to 110°C comprising a copolymer of ethylene and a vinyl ester or alkyl acrylate; a third layer comprising at least 50 percent by weight of copolymer of ethylene with at least one α -olefin or at least one vinyl ester or blends thereof, and a second layer between said first and third layers; said second layer comprising a vinylidene chloride copolymer, a nylon or a copolymer of ethylene with a vinyl alcohol; said film having a ram puncture force of at least 120 Newtons, and a total energy absorption of at least 1.20 Joules.

65. A film, as defined in claim 64, wherein said maximum puncture force is at least 150 Newtons.

66. A film, as defined in claim 64, wherein said maximum puncture force is at least 200 Newtons.

67. A film, as defined in claim 64, wherein said film has a total energy absorption of at least 1.50 Joules.

68. A film, as defined in claim 64, wherein said film has a total energy absorption of at least 2.0 Joules.

69. A film, as defined in claim 64, wherein at least one of said first, second, and third polymers comprises an interpolymer.

70. A film, as defined in claim 64, wherein at least one interpolymer comprises said first and second polymers.

71. A film, as defined in claim 64, wherein said first layer is a surface heat sealing layer.

72. A polymer blend of at least three copolymers comprising:

20 to 85 weight percent of a first polymer having a melting point of 80 to 98°C comprising at least one copolymer of ethylene and hexene-1;

5 to 35 weight percent of a second polymer having a melting point of 115 to 128°C comprising at least one copolymer of ethylene and at least one α -olefin; and

10 to 50 weight percent of a third polymer having a melting point of 60 to 110°C comprising at least one copolymer of ethylene and a vinyl ester or an alkyl acrylate; wherein said first and second polymers have a combined weight percentage of at least 50 weight percent, said weight percentage being based upon the total weight of said first, second and third polymers.

73. A blend, as defined in claim 72, wherein said first polymer is present in an amount of 25 to 45 weight percent, based upon the total weight of the first, second and third polymers.

74. A blend, as defined in claim 72, wherein said first polymer is present in an amount of 30 to 40 weight percent, based upon the total weight of the first, second and third polymers.

75. A blend, as defined in claim 72, wherein said first polymer is present in an amount of 45 to 85 weight percent, based upon the total weight of the first, second and third polymers.

76. A blend, as defined in claim 72, wherein at least one of said first, second, and third polymers comprises an interpolymer.

77. A blend, as defined in claim 72, wherein said first and second polymers comprises an interpolymer.

78. A flexible film comprising at least one layer comprising the blend of claim 72.

79. A flexible film, as defined in claim 78, wherein said film comprises:

Sub
A5
a heat sealing surface layer comprising a polymer selected from the group consisting of:
(a) at least 50% by weight of a copolymer of propene and at least one α -olefin selected from the group consisting of ethylene, butene-1, methylpentene-1, hexene-1, octene-1 and mixtures thereof having a propene content of at least 60 wt. %, and (b) at least 50% by weight of a copolymer of ethylene and at least one α -olefin selected from the group consisting of propylene, butene-1, methylpentene-1, hexene-1, octene-1 and mixtures thereof having a melting point of at least 105°C and a density of at least 0.900 g/cm³;

an intermediate layer;

a core layer;

an outer protective surface layer;

wherein at least one of said intermediate and said outer protective layers comprise said blend defined in claim 72, and said core layer is disposed between said intermediate and said outer protective layers, and said film has a hot water seal strength of at least 200 seconds at 95°C.

80. A process for making biaxially stretched, heat shrinkable film comprising:

extruding a melt plastified primary tube comprising 20 to 85 weight percent of a first polymer having a melting point of 80 to 98°C comprising at least one copolymer of ethylene and hexene-1;

Sub
B9
5 to 35 weight percent of a second polymer having a melting point of 115 to 128°C comprising at least one copolymer of ethylene and at least one α -olefin; and

10 to 50 weight percent of a third polymer having a melting point of 60 to 110°C comprising at least one copolymer of ethylene and a vinyl ester or an alkyl acrylate; wherein said first and second polymers have a combined weight percentage of at least 50 weight percent, said weight percentage being based upon the total weight of said first, second and third polymers;

cooling said primary tube;

reheating said cooled tube to a draw point temperature of 68 to 88°C;

biaxially stretching said tube to provide a transverse direction circumference of at least 2½ times the circumference of said primary tube and a machine direction length of at least 2½ times the length of a corresponding segment of said primary tube, and cooling said biaxially stretched tube to form a biaxially stretched, heat shrinkable film having a film thickness less than 10 mil (254 microns).

81. A process, as defined in claim 80, wherein said draw point temperature is of 65 to 79°C.

82. A process, as defined in claim 80, wherein said resultant film has a ram puncture force of at least 70 Newtons, a ram puncture stress of at least 110 MPa, and a tear propagation strength "x" such that $10 \leq x \leq 40$ grams per mil in each of the machine and transverse directions or $x < 25$ grams per mil in at least one of the machine and transverse directions.

83. A process, as defined in claim 80, wherein said resultant film has a ram puncture force of at least 120 Newtons, and a total energy absorption of at least 1.20 Joules.

84. A process, as defined in claim 80, wherein a multilayer primary tube is coextruded having a first inner surface layer of said tube comprising said first, second and third polymers as defined in claim 80, and further comprising at least one additional thermoplastic polymeric layer.

85. A process, as defined in claim 84, wherein a multilayer primary tube is made by extruding a tube comprising said first, second and third polymers as defined in claim 80, and coating laminating onto said tube at least one additional thermoplastic polymeric layer prior to biaxially stretching said tube.

86. A process, as defined in claim 84, wherein a multilayer primary tube is made by coextrusion or coating lamination and said resultant biaxially stretched film comprises:

a heat sealing surface layer comprising a polymer selected from the group consisting of:

(a) at least 50% by weight of a copolymer of propene and at least one α -olefin selected from the

group consisting of ethylene, butene-1, methylpentene-1, hexene-1, octene-1 and mixtures

thereof having a propene content of at least 60 wt. %, and (b) at least 50% by weight of a

copolymer of ethylene and at least one α -olefin selected from the group consisting of propylene, butene-1, methylpentene-1, hexene-1, octene-1 and mixtures thereof having a melting point of at least 105°C and a density of at least 0.900 g/cm³;

an intermediate layer;

a core layer comprising at least 80% by weight (based on said third layer's weight) of at least one copolymer of: EVOH; or vinylidene chloride with from 2 to 20 weight percent (based on said copolymer's weight) of vinyl chloride or methyl acrylate; and

an outer protective surface layer;

wherein at least one of said intermediate and said outer protective layers comprise said blend defined in claim 80, and said core layer is disposed between said intermediate and said outer protective layers, and said film has a maximum ram puncture force of at least 100 Newtons, a hot water puncture resistance of at least 100 seconds at 95°C and a hot water seal strength of at least 200 seconds at 95°C.

87. A biaxially stretched, heat shrinkable, multilayer film useful for food processing and packaging having at least four layers comprising:

a first heat sealing surface layer comprising a polymer or blend of polymers selected from the group consisting of: (a) at least 50% by weight of a copolymer of propene and at least one α -olefin selected from the group consisting of ethylene, butene-1, methylpentene-1, hexene-1, octene-1 and mixtures thereof having a propene content of at least 60 wt. %, and (b) at least 50% by weight of a copolymer of ethylene and at least one α -olefin selected from the group consisting of propylene, butene-1, methylpentene-1, hexene-1, octene-1 and mixtures thereof having a melting point of at least 105°C and a density of at least 0.900 g/cm³;

a second polymeric layer comprising (a) from 10 to 85% of a first copolymer of

ethylene and at least one C₃-C₈ α-olefin, said first copolymer having a melting point of 55 to 98°C; (b) from 5 to 60% of a second copolymer of ethylene and at least one C₄-C₈ α-olefin, said second copolymer having a melting point of 115°C to 128°C, (c) from 0 to 50% of a third copolymer having a melting point of 60 to 110°C of ethylene with a vinyl ester or alkyl acrylate, wherein said first and second copolymers have a combined weight percentage of at least 50 weight percent, said weight percent being based upon the total weight of said layer;

a third layer comprising at least 80% by weight (based on said third layer's weight) of at least one copolymer of vinylidene chloride with from 2 to 20 weight percent (based on said copolymer's weight) of vinyl chloride or methyl acrylate; and

a fourth polymeric layer comprising (a) from 10 to 85% of a first copolymer of ethylene and at least one C₃-C₈ α-olefin, said first copolymer having a melting point of 55 to 98°C, (b) from 5 to 60% of a second copolymer of ethylene and at least one C₄-C₈ α-olefin, said second copolymer having a melting point of 115°C to 128°C, and (c) from 0 to 50% of a third copolymer having a melting point of 60 to 110°C of ethylene with a vinyl ester or alkyl acrylate, wherein said first and second copolymers have a combined weight percentage of at least 50 weight percent, said weight percent being based upon the total weight of said layer; and

wherein said film has a shrinkage value at 90°C of at least 40% in at least one of the machine and transverse directions, and said film has a tensile seal strength of at least 400 g/cm at 88°C.

88. A film, as defined in claim 87, wherein said film has a maximum ram puncture force of at least 70 Newtons.

89. A film, as defined in claim 87, wherein said film has a maximum ram puncture force of at least 110 Newtons.

90. A film, as defined in claim 87, 88 or 89, wherein said film has a hot water puncture resistance of at least 20 seconds at 95°C.

91. A film, as defined in claim 87, wherein said film has a hot water puncture resistance of at least 40 seconds at 95°C.

92. A film, as defined in claim 87 or 88, wherein said film has a hot water puncture resistance of at least 60 seconds at 95°C.

93. A film, as defined in claim 87 or 89, wherein said film has a hot water puncture resistance of at least 100 seconds at 95°C..

94. A film, as defined in claim 87, 88 or 89, wherein said film has a hot water seal strength of at least 200 seconds at 95°C.

95. A film, as defined in claim 87, 88 or 89, wherein said film has a hot water seal strength of at least 300 seconds at 95°C.

96. A film, as defined in claim 87, wherein said melting point of said first heat sealing surface layer polymer (b) is at least 115°C.

97. A film, as defined in claim 87, wherein said film has a thickness less than 175 microns.

98. A film, as defined in claim 87, wherein said film has a thickness between 50 to 150 microns.

99. A film, as defined in claim 87, wherein said film has a haze value of less than 10% and a gloss at 45° of at least 70 Hunter units.

100. A film, as defined in claim 87, wherein said film has an oxygen transmission rate of less than 45 cm³/m² for 24 hrs. at 1 atm. at 23°C.

101. A film, as defined in claim 87, wherein said first copolymer of at least one of said second and fourth layers has a density less than 0.900 g/cm³.

102. A film, as defined in claim 87, wherein said first copolymer of both said second and fourth layers has a density less than 0.900 g/cm³.

sub 103. A film, as defined in claim 87, wherein said ~~third copolymer of both said second and fourth layers comprises 4 to 18 % (by weight of said copolymer) of a vinyl ester or alkyl acrylate.~~

503
B13

104. A film, as defined in claim 87, wherein: (a) in at least one of said second and fourth polymeric layers said first copolymer comprises at least one copolymer having a melting point of 80 to 98°C of ethylene and hexene-1 and is present in an amount of from 20 to 85 weight percent, and wherein (b) said second copolymer has a melting point of 115 to 128°C and is present in an amount of 5 to 35 weight percent; and (c) said third polymer having a melting point of 60 to 110°C is present in an amount of 10 to 50 weight percent, based upon the layer weight.

105. A film, as defined in claim 87, wherein both of said second and fourth polymeric layers comprise:

(a) 20 to 85 weight percent of a first copolymer having a melting point of 80 to 98°C comprising at least one copolymer of ethylene and hexene-1;

(b) 5 to 35 weight percent of a said second copolymer having a melting point of 115 to 128°C; and

(c) 10 to 50 weight percent of said third polymer having a melting point of 60 to 110°C.

106. A film, as defined in claim 42, 63, or 96, wherein said melting point of said first heat sealing surface layer polymer (b) is at least 115°C.

107. A film, as defined in claim 104 or 105, wherein said copolymer of ethylene and hexene-1 is present in an amount of 45 to 85% of said layer.

108. A film, as defined in claim 104 or 105, wherein said copolymer of ethylene and hexene-1 is present in an amount of 20 to 45%.

Add D3